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Potential ecological risk of heavy metals in surface sediments from the Aden coast, Southern Yemen

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Abstract: *Eleven approaches were employed to evaluate degree of heavy metals pollution in surface sediment from the Aden coast, Southern Yemen, was investigated by applying a set of complementary sediment quality assessment methods: (1) Comparison with the background value, (2) Sediment Quality Guidelines (SQG), (3) Toxicity guidelines for adverse biological effects, (4) Enrichment factor (EF), (5)Geo-accumulation index (Igeo), (6) Quantification of contamination index (QoC), (7) Contamination factor (Cf), (8) Degree of contamination (Dc), (9) Pollution Load Index (PLI), (10) Potential ecological risk factor (Er), and (11) Potential ecological risk index (RI). The heavy metal concentrations in the Aden coast sediments ranged from 0.6–2.92 $\mu g\ g^{-1}$ for Cd, 9.7-26.4 $\mu g\ g^{-1}$ for Co, 12.6-40.9 $\mu g\ g^{-1}$ for Cr, 3.3-55.3 $\mu g\ g^{-1}$ for Cu, 1061-3663 $\mu g\ g^{-1}$ for Fe, 47.8- 394.6 $\mu g\ g^{-1}$ for Mn, 3.9-30.3 $\mu g\ g^{-1}$ for Ni, 13.6-46.9 $\mu g\ g^{-1}$ for Pb, and 32.3-97.2 $\mu g\ g^{-1}$ for Zn. When the results of this study were compared to the background values, for Cd the concentration were exceeded the background values in study area. Pb were more than the background value in all sites, except coast of Abyan & Al-Hiswah. It was observed that the coasts of Al-Hiswah, Sira Island, Kobagen, and Fuqum were moderate polluted for Cr. The contamination levels of Pb were moderately polluted in the Labor island and al-Ghadir. The Ni were moderately polluted in the Fuqum coast. According to the ERL and TEL values, The concentration of Cd were exceeded ERL value in the all sites, 77.8% of total sampling sites were exceeded ERL value. Ni, Pb and Cu levels were exceeded TEL value (44.4%, 33.3%, 11% of total sampling sites, respectively). Based on the geo-accumulation index, the Co, Zn, Cu, Cr, Ni, Mn, and Fe levels were graded as non-contamination, the level of Pb metal is moderately to unpolluted, while those of Cd are moderately polluted in the all sites, except of Abyan coast is unpolluted. The EF results demonstrated that the metals in the study area have been enriched (anthropogenic additions), except al-Khissa coast that the Ni and Mn in sediment is originated predominantly from lithogenous material. The results of the present study were highly enriched in Cd and significantly enriched in Lead. According to the contamination factor and quantification of contamination calculations, Ni, Mn, Cr, Cu, Zn, and Co were derived mainly from natural processes and geogenic sources and were related to the exposure of the Earth's crust material, while the increased values of Cd, and Pb were ascribed to anthropogenic activities. The elevated values identified for Cd, and Pb might be related to human activities including sewage effluents, fishing activities, human refuse, shipping, transportation, fuel smuggling, and industrial wastewater. Dc values indicate a moderate degree of contamination in all study area, except at sites Amran, al-Hiswah and Abyan (low degree of contamination). The potential ecological risk coefficient (Er) of Pb, Co, Cu, Ni, Cr, Zn, and Mn were all lower than 40, which belong to low ecological risk, while Cd fell within moderate ecological risk; considerable risk category and high risk.The total ecological risk index (RI) of eight heavy metals in the study area were ranged between 80 and 299 thus falling within the class of low to moderate ecological risk.*

Keywords: *heavy metals, assessment,; risk index, sediment, Gulf of Aden*

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I. Introduction

Heavy metal pollution in the marine environment is of great concern around the world [1][2][3], because of their toxic effects, long-term persistence, and bioaccumulation characteristics [4] [5][6][7]. Heavy metals are of considerable environmental concern due to their toxicity, wide sources, non-biodegradable properties and accumulative behaviors [8]. Metals enter into the aquatic environment from natural processes and anthropogenic activities [4][9][10] [11][12] .

Many researchers have studied the heavy metal contamination in the Aden coast of Yemen [13] [14][15][16][17][18][19][20][21][22][23][24][25]. However, no information is available about Potential ecological risk assessment in this coastal sediment. Sampling in the study area for previous studies more than seven years. Saleh's study [18] included the assessment of pollution and geochemical form of heavy metals, used criteria to evaluate pollution such as comparison with background levels and sediment quality guidelines according to international standards, Toxicity guidelines of heavy metals, Enrichment Factors, enrichment factor, pollution degree, Application of principal component analysis and cluster analysis. The hot spots in the study area were determined by the SQI, PLI and Dc. It showed that the highest index was recorded at the fishing harbor and Al-Hiswah, the most polluting elements are Pb, Cr, Ni and Zn. The results reflected the dangerous of Pb in the study area, Pb showed strong affinity for exchangeable and carbonate fractions in the sampling sites, reached to more than 40 % of the total Pb at Sira site. The risk assessment of metals in the Aden coasts, Gulf of Aden, show can be arranged as the following: Pb > Co > Mn > Ni > Zn > Cu > Cr > Fe [18]. Most marine pollution in the Aden port is caused by discharge of untreated waste water of desalination plant, electrical power station, refinery plant, textile industry, oil spill from the oil pipes, as well as domestic wastewater [18].

This study is an extension of Saleh's study in 2007 with the addition of four new areas namely al-Khissa, al-Ghadir, Kobagen and Amran, In addition to assessing cadmium pollution.

The aim of this study was to:

(1) provide the concentration and distribution of some heavy metals in surface sediments from the Aden coast, Yemen.

(2) evaluate the pollution levels of some heavy metals was assessed with the application of eleven different indices, The background values, Sediment Quality Guidelines (SQG), Toxicity guidelines for adverse biological effects, Enrichment factor (EF), Geo-accumulation index (Igeo), Quantification of contamination index (QoC), Contamination factor (Cf), Degree of contamination (Dc), Pollution Load Index (PLI), Potential ecological risk factor (Er) and the Potential ecological risk index (RI).

II. Materials And Methods

2.1. Study area and sampling

Aden city is located at the southern part of Yemeni coast at Gulf of Aden at the coordination 12° 28' - 12° 57' N and 44° 27' - 45° 07' E. It is located at the south west tip of Yemen and the Arab peninsula. Mid-way between Europe and Far East, Aden lies on major world trading route through the Suez canal. It is one of the largest natural harbors in the world with an area of about 70 km^2 of sheltered water surrounded by Jebel Shamsan, khoremakser, and the shore which extends to the hills of Little Aden. Aden contained a series of communities stretching around a well protected bay; these include Crater, Ma'alla, Tawahi, Khormaksar, Shikh-Othman, Al-Mansura, Dar Saad, and Little Aden. Most of the inland and southwest areas of Aden are sparsely occupied. The airport is located in khormaksar, the harbor dominates ma'alla and Tawahi, Al-Hoswah Power station and industrial zone in Madinat Al-Shaab and the oil refinery and oil harbor are in Little Aden [18].

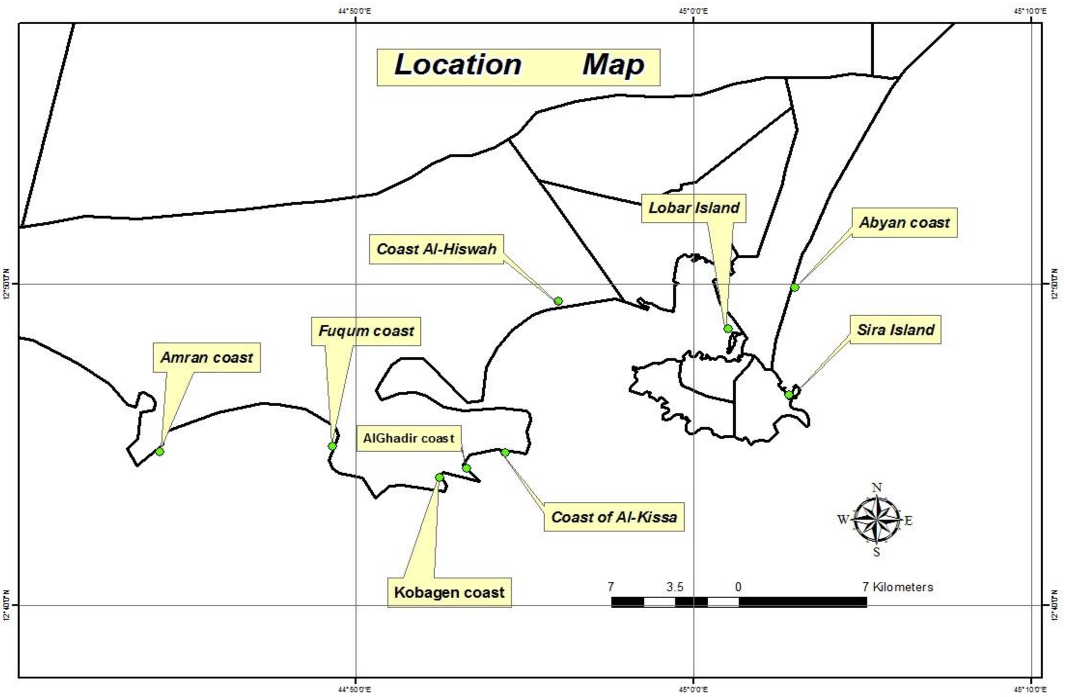


Figure 1: Study Area and Sampling Sites

2.2. Sampling and Preparation

Superficial sediment samples were collected in July - August, 2014 from Nine sampling stations along the coastal area of Aden, "fig." (1) and Table (1). Samples were transferred to plastic bags and placed in a cooler at 4°C, transported to the laboratory. Sediments were dried at 80 °C in the incubator till fixed weight. The dried sediments were filtered using 100 µm mesh.

Table (1) Sampling locations description

Name of Site	Site No.	Latitude	Longitude	Site description
Sira Island	A1	12° 48' 36" N	45° 01' 06"E	Population pressure, Sewage effluents, fishing activities, tourism activities and the urban activities, transportation
Abyan coast	A2	12° 50' 24" N	45°20' 47" E	Sewage effluents, tourism activities and the urban activities, transportation,
Labor Island	A3	12° 48' 36" N	45°10' 60" E	Industrial and municipal waste water, used the store old, damaged ships and boats, transportation.
Al-Hiswah	A4	12° 49' 27" N	44°55' 59" E	Power and desalination plants, runoff, oil spill from the oil pipes, transportation.
al-Khissaa	A5	12° 44' 45" N	44°54' 26" E	Sewage effluents, fishing activities, tourism activities and the urban activities
al-Ghadir	A6	12° 44'16" N	44°53'16" E	Industrial facilities (near from oil refinery), fishing activities, tourism activities and the urban activities of the coastal cities.
Kobagen	A7	12° 43' 59" N	44°52'29" E	Untapped nature, Low Tourism activities.
Fuqum	A8	12°45' 40" N	44°49'36" E	Sewage effluents, fishing activities, tourism activities and the urban activities.
Amran	A9	12° 45' 52" N	44°44'52"E	Sewage effluents, fishing activities, tourism activities and the urban activities.

2.3. Metal analysis

Total metals analyses of sediments were determined according to Oregioni and Aston[26]. An exact weight (0.5g) of dry sample (drying at room temperature) of sediment was completely digested in Teflon vessels using a mixture of HNO_3, HF and $HClO_4$ (3:2:1) at 80°C. The final solution was diluted to 25 ml with double deionized distilled water. All digested solutions were analyzed in duplicate using the atomic absorption spectrophotometer (Vario 6) and the results were expressed in $\mu g\ g^{-1}$; dry weight.

2.4. Quality Assurance and Quality Control

All reagents used were of analytical grade (Merck), a replicate analysis for samples showed a good accuracy. To remove any contamination, all glassware and plastic vessels were washed with diluted nitric acid solution and deionized water and dried. Blanks were treated identically, using the same reagents for testing the precision**.** In order to check for the quality of the method applied for the analysis of heavy metals, the accuracy of the analytical method was estimated by analyzing sediment standard reference material (IAEA-405) [26]. The recovery of the selected metals ranged from 92 to 110% and the measurements of precision was within 10% RSD.

2.5. Assessment methodology of sediments contamination

2.5.1. Sediment Quality Guidelines (SQG)

To evaluate the level of contamination, sediments were categorized into three classes,: non-polluted, moderately polluted and heavily polluted, based on the SQG of US EPA [27]. Another classification system is the Hong Kong environmental Protection Department Classification system [28]. In this system 4 classes are used to classify the sediment quality. The first class showed to be classified as uncontaminated sediment (Class A). Whereas, the second class represented (Class B) slightly contaminated sediment. The third and the fourth class were considered as moderately and seriously contaminated (Class C & Class D), respectively, Table (2).

2.5.2. Toxicity guidelines of heavy metals

Incidence of adverse biological effects within range of chemical concentrations in marine and estuarine sediments by Long et al., [29], Table (2). The chemical concentrations corresponding to the 10^{th} and 50^{th} percentiles of adverse biological effects were called the effects-range low (ERL) and ERM guidelines, respectively. Another sediment quality guideline which is most widely used to assess the ecotoxicology of sediments is the threshold effects level [TEL] and probable effects level [PEL]. Where ERL and TEL are the concentrations below the adverse effects are expected to occur only rarely, whereas, ERM and PEL represented chemical concentration above the adverse effects are likely to occur.

2.5.3. Geo-accumulation Index (*Igeo*)

The geoaccumulation index (*Igeo*) to assess contamination level of metal in sediments of Aden coast. It is a quantitative measure of the degree of pollution in aquatic sediments. The geoaccumulation index is determined following Müller (1979)[30] as:

$$I_{geo}=log_2(C_n /1.5\ B_n)$$

where *Cn* is the measured concentration of the heavy metal (n) in the sediment, *Bn* is the geochemical background value in the average shale values for metals given by Turekian and Wodepoh [31]; 1.5 is background matrix correction factor due to lithogenic effects [32]. Based on the *Igeo* values, Müller [33] distinguished seven classes of sediments as presented in Table (3).

2.5.4. Enrichment factor (EF)

Enrichment factor is used to assess the degree of anthropogenic influence on element load in the sediments [34], and also to differentiate between elements originating from the natural or anthropogenic activities [35]. According to Ergin *et al.,* [59] the metal enrichment factor (*EF*) defined in this study as the concentration ration of metal to iron in the sample compared to the ratio in the natural background, average shale standards of metals described by Turekian and Wodepoh [31] were taken as geochemical reference values in the present study Table (3).

2.5.5. Quantification of contamination (*QoC%*)

The quantification of contamination index (*QoC*) mainly quantifies the anthropogenic concentration of a metal employing the concentration of the background metal to represent the lithogenic metal [36]. This is calculated in accordance with Eq. :

$$QoC\ (\%) = (X – Xe/X) \times 100$$

Xe: average concentration of the metal in background [36], Table (3). The values of this index are mainly expressed as percentage, demonstrating the magnitude of lithogenic and anthropogenic impacts [37].

2.5.6. Contamination factor (CF) and Degree of contamination (Dc)

The contamination factor (CF) and the degree of contamination (Dc) were used to determine the contamination status of study area. The formula and terminology for describing contamination factor (CF) and degree of contamination (Dc) [38] are shown in Table (3).

2.5.7. Assessment according to Pollution Load Index (PLI)

The pollution load index (PLI) is another simple method to assess the level of pollution in sediments. In this study, *PLI* is determined the method proposed by Tomlinson *et. a*l., [39], Table (3).

2.5.8. Ecological Risk Assessment (Er) and Potential Ecological Risk Factor (Risk Index:RI)

The purpose of ecological risk assessment is to assess ecological effects of human activities through scientifically credible evaluation (chemical assessment and individual bioassay) to protect and manage the environment. The assessment of ecological risks of heavy metals in the sediment samples was done using the Ecological Risk Assessment (*Er*) and Risk Index (*RI*) proposed by Hökanson [38] and reported in Huang *et al.,* [40], Table (3).

This method not only reflects the potential ecological harm from heavy metals in single specific sediment, but also considers the integrated ecological effect of a variety of heavy metals. What is more, the method can quantitatively differentiate the potential ecological risk of heavy metals by the calculated index values. It is one comprehensive index that can represent the influence degree of heavy metals on the ecological environment [41].

Potential ecological risk index method, *PERI* was used to evaluate the harm of heavy metals in the sediment samples. which was originally proposed by Hökanson, [38]. The value of *RI* can be calculated by the following formulas :

$$Er_i = Tr_i \times CF$$

$$RI = \Sigma Er$$

where *RI* is the sum of potential risk of individual heavy metal; *Er* is the potential ecological risk index for single heavy metal pollution; Tr_i is the toxic-response factor for a given heavy metals (i.e. Cd = 30, Pb = Cu = Ni = Co= 5, Cr = 2, Zn, Mn = 1) [38] [42]; *CF* is the contamination factor of a single element of "i"; *Ci* is the measured concentration of heavy metals in samples; *Cn* is the reference value which is the concentration of heavy metal in the background value. Average shale values [31], and average crustal abundance [43] were commonly used to provide elemental background concentrations [44]. The average shale background concentration of global sediments [31] is selected as the reference baselines in this study.

III. Results And Discussions

3.1. Distribution of Heavy metals in sediment

The concentrations of the nine metals that were analyzed (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn) in the surface sediments in the nine sites of Aden coast are listed in "figures" (2) (3) and (4). Among the 9 elements studied, concentrations of Fe, Mn, Zn, Pb and Cr were higher, where as lower concentrations of Co, Cu, Ni, and Cd were observed in the different sampling sites. The highest levels of Cr, Zn, and Mn were recorded at Sira Island (32.95; 78; 320 µg g^{-1}, respectively), highest values of Cd, and Cu were detected at al-Khissa site (2.86 µg $g^{-1}$and 33.2 µg g^{-1}, respectively), while the maximum value for Pb, Ni, Co, and Fe were detected at al-Ghadir, Fuqum, al-Hiswah and at Abyan coast (46.45µg g^{-1};30 µg g^{-1} ; 20.55 µg g^{-1}; 3634 µg g^{-1}, respectively). On the other hand, the lowest concentrations were observed at Abyan coast (0.7 µg g^{-1} Cd; 10.3 µg g^{-1} Co; 35 µg g^{-1} Zn), al-Khissa (85 µg g^{-1} Mn; 4.1 µg g^{-1} Ni), Amran coast(19.25 µg g^{-1} Cr; 6.1 µg g^{-1} Cu), Kobagen (1197 µg g^{-1} Fe) and 15.3 µg $g^{-1}$for Pb at Labor Island.

Compared to the results of a previous study with those reported in the literature concluded that the concentrations observed in the Aden coasts were lower or higher than those recorded in the other studies, Table (4). Concentrations of metals reported in the present study were relatively magnitudes lower than the metal levels reported for the nearby areas in a previous study [18] [23], and southwest coast of Spain [45]. The range observed of Cd, Ni, Mn, Fe and Pb in the present study were lower than those reported for the sediments of Egyptian Red Sea Coast [46] and Ni, Cr and Fe were lower than those recorded in coastal sediments in the Gulf and Gulf of Oman (Ras Al-Yein, Oman and Akkah Beach, Abu Dhabi) [47]. However, the results of a previous study were much higher than those reported for the sediments of Red Sea in front of Yemen [48], and Tuticorin coast India [49]. The range observed of Pb, Cr, Zn and Mn in the present study were higher than those reported for the sediments of Hadramout coast, Yemen [9]. The levels of Cd, Pb, Zn, and Cu were more than those recorded in the Ras Al Yei, Oman and Akkah Beach, Abu Dhabi [47]. In general, the results obtained in this study were in the range observed in other reported for the nearby areas in a previous study.

3.2 Comparison with the background value

The background values of different metals were defined according to average continental shale [31], which are shown in Table (2) and figures (2) (3) and (4). For Cd the concentration were exceeded the background values in study area. Pb were more than the background value in all sites, except sites A2 and A4 (Coast of Abyan & al-Hiswah), our results are in similar with those found recorded by Saleh [18]. The concentrations of Cu, Co, Cr, Ni, Zn, Fe and Mn were less than the background value for all sites, except al-Hiswah and Fuqum for Co.

The background values of different metals were defined according to international standard: Cd, Pb, and Cr [50] [51] [46], Zn and Cu [52] [18]; Fe, Mn and Ni [53] [45], and Co [18][54], which are shown in Table (2). For Cd, Pb and Cr the concentrations were exceeded the background values in all sites, our results are in similar with those found recorded by Saleh at gulf of Aden[18]. The concentrations of Fe and Mn were less than the background value for all sites. For Cu, Co, Ni, and Zn the concentrations were less than the background level in all sites, except coast of al-Khissa for Cu, Fuqum coast for Ni, Sira island for Co and Labor island, Sira island and al-Ghadir coast for Zn.

3.3. Assessment According to Sediment Quality Guidelines (SQG)

Numerous sediment quality guidelines are used to protect aquatic biota from the harmful and toxic effects related with sediment bound contaminants [55]. These guidelines evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and are designed for the interpretation of sediment quality. They are also used to rank and prioritize contaminated areas for further investigation [56]. The National Standard of China (NSC) GB18668-2002 [57], has defined three grades of marine sediment, in which the content of some heavy metals is regarded as parameters used to classify marine sediments quality, Table (2). According to this criterion, the first class quality is suitable for mariculture, nature reserves, and endangered species reserves, and leisure activities such as swimming; the second class quality can be used for industry and tourism sites; and the third class can only be used for harbors.

To evaluate the level of contamination, sediments were classified as: non-polluted, moderately polluted and heavily polluted, based on the SQG of US EPA [27], Table (2) and figures (2) (3) and (4). It was observed that the coasts of al-Hiswah, Sira Island, Kobagen, and Fuqum were moderately polluted for Cr. The contamination levels of Pb were moderately polluted in the Labor island and al-Ghadir. The Ni were moderately polluted in the Fuqum coast. In general, all metals studied have not reached the point of severe pollution (Heavily polluted).

Comparing the sediment of the present study with classification system from Hong Kong environmental Protection Department (EPD) Classification system [28], the range value of the cadmium were considered as moderately and seriously contaminated (Class C and Class D), while the range value for Copper, Nickel, Lead, and Zinc concentrations showed to be classified as uncontaminated (Class A) to moderately contaminations (Class B), Table (2).

3.4. Toxicity guidelines of heavy metals

Many metals are highly toxic and have chronic effects on living organisms. Elevated concentrations of metals in sediments could cause detrimental effects to benthic organisms as well as other aquatic organisms. Some toxicity guidelines of trace metals are given in Table (2). The concentration of Cd were exceeded ERL and TEL values in the all sites, except sites 2A and 4A were less than the ERL values. Sites A3, A5 and A6 exceeded the TEL for Pb. Ni level exceeding TEL for sites A1, A3, A6 and A8 "fig" (2). Site A5 exceeded the TEL for Cu "fig" (3). another metals concentrations were below the TEL value represent concentrations, which are not expected to cause any adverse biological effects "fig" (4). According to values Saleh [18], the concentrations of some trace metals (Pb, Cr, Ni and Zn) in the Gulf of Aden sediments more than TEL. Concentrations equal/or above the ERL, but below the ERM, indicates a possible range in which effects would occasionally occur. The concentrations equivalent to and above ERM values indicates that the effects would occur frequently. The concentrations equal/or above the TEL, but below the PEL probable effect level represent a range of concentrations within which effects may occasionally occur on sensitive organisms, but there is only a slight risk. Concentrations equal/or above PEL value represent a probable-effects range within which adverse biological effects would frequently occur [29] [18] [58] [46] .

3.5. Enrichment factor (EF)

Enrichment factor (EF) is a common method used to study the enrichment degree of metals in sediments and soil. For a better estimation of anthropogenic input of metal in the surface sediments of the Aden seashore, the metal profiles were normalized to Fe. The reason for choosing Fe instead of other elements is its wide distribution in Crust or in the average shale values for metals. In this study, the coefficient of enrichment was determined according to Ergin et al., [59], Table (3), and natural background values of metals were used described by Turekian and Wodepoh [31], Table (2). The *EF* values were < 2 indicate that the metal is entirely from crustal materials or natural processes; whereas *EF* values > 2 suggest that the sources are more likely to be anthropogenic [34] [60] [61]. The enrichment factor (*EF*) of the various in the sediment of Aden seashore are presented in Table (5). All of studied samples showed valuable anthropogenic additions of all studied metals, except al-Khissa coast that the Ni and Mn in sediment is originated predominantly from lithogenous material. For Aden seashore *EF* mean values of metals have the order $EF_{Cd} > EF_{Pb} > EF_{Co} > EF_{Zn} > EF_{Cu} > EF_{Cr} > EF_{Mn} > EF_{Ni}$. The difference in EF values may be due to the difference in the magnitude of input for each metal in the sediment and/or the difference in the removal rate of each metal from the sediments [46]. The results of the present study showed that Aden seashore sediments were highly enriched in Cd and significantly enriched in Lead.

3.6. Geo-accumulation Index (Igeo)

The geo-accumulation indexes calculated for the sediments of Aden coast are summarized in Table (6). According to Müller’s scale [30], the geo-accumulation indexes of Co, Zn, Cu, Cr, Ni, Mn, and Fe are less than zero (*Igeo*<0), suggesting that the study area has not been polluted overall by these metals. Pb metal is moderately to unpolluted, Cd are moderately polluted in the all sites, except of Abyan coast is unpolluted. Among the studied elements, Cd had the highest *Igeo* values, suggesting the sediments has been moderately polluted with this metal. For Aden seashore, the mean *Geo-accumulation Index* of metals represented the decreasing order **Cd > Pb > Co** > Ni > Zn > Cu >Cr > Mn >Fe

3.7. Quantification of contamination (QoC%)

Quantification of contamination (*QoC*, %) values of metals in the sediments of Aden coast are given in Table (7). According to the quantification of contamination calculations, Ni, Mn, Cr, Cu, Zn, and Co were derived mainly from natural processes and geogenic sources and were related to the exposure of the Earth’s crust material, except for cobalt metal in four sites (al- Hiswah, al-Ghadir, Fuqum, and Amran), were related to anthropogenic sources, while the increased values of Cd, and Pb were ascribed to anthropogenic activities in all sites. Overall average quantification of contamination of metals followed the order **Cd > Pb > Co** > Zn > Mn > Cr > Cu > Ni > Fe

The elevated values identified for Cd, and Pb might be related to human activities including sewage effluents, fishing activities, human refuse, shipping, transportation, fuel smuggling, and industrial wastewater.

3.8. Contamination factor (CF)

The values obtained from the contamination factor (*CF*) shown in Table (3). In the present study, the values of the contamination factor (*CF*) for Zn, Ni, Cu, Cr and Mn, they were found to be low contamination in all study areas, Table (8).The concentration of **cadmium** is indicating very high contamination at sites A5,A6 and A7; considerable contamination in the A1,A3,A4,A8,A9 sites and site A2 (Abyan Coast) indicate that it is moderate contamination. The **lead** metal is indicating moderate contamination in the all sites, except site A2 (Abyan coast) and site A4 (al-Hiswah coast) indicate that it is low contamination. The concentration of **Cobalt** were within the low contamination in the all sites, except sites A4 (al-Hiswah) and A8 (Fuqum) were within the moderate contamination. This might be related due to industrial waste from Power and desalination plants and run-off from Lahij governorate to al-Hiswah site, which including disposal of liquid effluents and terrestrial runoff, as well as atmospheric deposition [18]. In general, The highest *CF* level was obtained for Cd (range:2.33-9.35;Average: 5.3), which registered a moderate degree to very high of contamination. The *CF* level was significantly high for Cd and Pb which suggests Cd and Pb high pollution due to anthropogenic activities (sewage effluents, fishing activities, damaged ships and boats, human refuse, shipping, transportation, fuel smuggling, and the industrial facilities). On the basis of the average *CF* values, the sediments may be considered to be contaminated by the metals investigated in the following order:

Cd> Pb> Co> Zn> Cu> Cr> Mn>Ni.

According to the contamination factor and quantification of contamination calculations, Ni, Mn, Cr, Cu, Zn, and Co were derived mainly from natural processes and geogenic sources and were related to the exposure of the Earth's crust material, while the increased values of Cd, and Pb were ascribed to anthropogenic activities. The elevated values identified for Cd, and Pb might be related to human activities including sewage effluents, fishing activities, human refuse, shipping, transportation, fuel smuggling, and industrial wastewater.

3.9. Degree of contamination (Dc)

The degree of contamination values of the metals studied and the ranges of *Dc* and their pollution grades and corresponding intensities are given in Table (8) and "fig." (5). *Dc* values indicate a moderate degree of contamination in all study area, except at sites A2, A4, A9 Abyan, al-Hiswah and Amran respectively (low degree of contamination). For study area, the degree of contamination of heavy metals represented the decreasing order:

al-Khissa>al-Ghadir>Labor Island>Kobagen>Fuqum>Sira Island>Amran>al-Hiswah >Abyan coast

3.10. Assessment according to Pollution Load Index (PLI)

The results of *PLI* are shown in Table (8) and "fig." (5). The results of our measurements show that the study area are not polluted.

The *PLI* is increasing according to the following order:

al-Khissa>al-Ghadir>Sira=Labor Island>Fuqum>Kobigan>Al-Hiswah>Abyan coast>Amran.

3.11. Ecological Risk Assessment (Er) and Potential Ecological Risk Factor (Risk Index:RI)

The results of evaluation on potential ecological risk factor (*Er*) and the potential ecological risk index (*RI*) are summarized in Table (9) and "fig." (5). The potential ecological risk coefficient (*Er*) of Pb, Zn, Cu, Cr, Co, Ni, and Mn were all lower than 40, which belong to low ecological risk, while Cd fell within moderate ecological risk (at site A2); considerable risk category (at sites: A1, A3, A4, A9) and high risk categories (at sites:A5 to A8).

The order of single factor potential ecological risk coefficient (Er) of heavy metals in surface sediments of the Aden coast was Cd>Pb>Co>Cu>Ni>Cr≥Zn>Mn.

The total ecological risk index (*RI*) of eight heavy metals in the study area were ranged between 80 and 299 thus falling within the class of low (sites:A1,A2,A4) to moderate ecological risk (sites:A3, A5-A9).

The order of total potential ecological risk coefficient (*RI*) of heavy metals in surface sediments of the Aden coast was A5>A6>A7>A8>A9>A3≥A1>A4>A2.

IV. Conclusion

The results of the present study cleared out that the sediment of the Aden coast were increased values of Cd, and Pb were ascribed to anthropogenic activities. The elevated values identified for Cd, and Pb might be related to human activities including sewage effluents, fishing activities, human refuse, shipping, transportation, fuel smuggling, and industrial wastewater.

Table (2) Statistical summary of the metal contents in study area (Average, Max., Min., SD) and Concentrations of metals in shale's and according to various guidelines and comparing with sediment quality guidelines (SQG)

Metal	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Average	1.59	16.16	24.87	15.75	2,771.7	214.9	14.50	28.15	54.70
Maximum	2.86	20.55	32.95	33.2	3633.5	320.3	30	46.45	77.95
Minimum	0.7	10.3	19.25	6.1	1196.5	85	4.05	15.3	35.3
SD	0.66	3.68	3.92	7.69	887	92.03	7.17	10.90	14.02
B value	0.38	20	17	20	5%	450	20	14	70
Average shale	0.3	19	90	45	47200	850	68	20	95
Non polluted	-	-	<25	<25	<17000	<300	<20	<40	<90
Moderately polluted	-	-	25-75	25-50	17000- 25000	300-500	20-50	40-60	90-200
Heavily polluted	>6	-	>75	>50	>250000	>500	>50	>60	>200
Class A	<0.1	-	<25	<10	-	-	<15	<25	<70
Class B	0.1–1.0	-	25–50	10–41	-	-	15–35	25–65	70–150
Class C	1–1.5	-	50–80	55–64	-	-	35–40	65–75	150–200
Class D	>1.5	-	>80	>64	-	-	>40	>75	>200
ERL	1.2	-	81	34	-	-	20.9	46.7	150
ERM	9.6	-	370	270	-	-	51.6	218	410
TEL	0.68	-	52.3	18.7	-	-	15.5	30.2	124
AET	-	-	2600	310	-	-	>140	150	340
PEL	4.2	-	140	108	-	-	43	112	270

B value: Background value, SD: Standard deviation, TEL: Threshold Effect Level, PEL: Probable Effect Level, ERL: Effects rang low, ERM: Effects range median, AET: Apparent Effects Threshold

Table (3) Sediment quality indices and their classification systems

Index	Equation	Classification	References
EF	$EF = \frac{(Metal / Fe)_{Sample}}{(Metal / Fe)_{Background}}$	*EF* values < 2 indicate that the metal is entirely from crustal materials or natural processes *EF*: 2 - 5 (moderate enrichment) *EF*: 5 - 20 (significant enrichment) *EF*: 20 - 40 (very high enrichment) *EF* > 40 (extremely high enrichment)	[59]
Igeo	$I_{geo}=log_2(C_n /1.5 B_n)$	*Igeo* < 0 Class 0 (unpolluted) 0 < *Igeo* < 1 Class 1 (unpolluted to moderately) 1 < *Igeo* < 2 Class 2 (moderately polluted) 2 < *Igeo* < 3 Class 3 (moderately to heavily polluted) 3 < *Igeo* < 4 Class 4 (heavily polluted) 4 < *Igeo* < 5 Class 5 (heavily to extremely polluted) *Igeo* ≥ 5 Class 6 (extremely polluted)	[30] [33] [62]
QoC%	$QoC (\%) = (X – Xe/X) \times 100$	*QoC* (%) = 0 (geogenic source) *QoC* (%) > 0 (anthropogenic magnitude)	[36] [37]
CF	$CF=C_a/ C_b$	CF < 1 (low CF) 1 ≤ CF < 3 (moderate CF) 3 ≤ CF < 6 (considerable CF) CF ≥ 6 (very high CF	[38] [63]
Dc	$Dc == \sum_{i=1}^{8} C_f^i$	*Dc* < 8 (low Dc) 8 ≤ *Dc* < 16 (moderate Dc) 16≤ *Dc* < 32 (considerable Dc) *Dc* ≥ 32 (very high Dc) indicating alarming anthropogenic contamination	[38] [64]
PLI	$PLI=\sqrt[n]{Cf1\ X\ Cf2\ X \ldots..X\ Cfn}$	PLI = 0 (background concentration) 0 < *PLI* ≤ 1 (unpolluted) 1 < *PLI* ≤ 2 (unpolluted to moderately) 2 < *PLI* ≤ 3 (moderately polluted) 3 < *PLI* ≤ 4 (moderately to highly polluted) 4 < *PLI* ≤ 5 (highly polluted) *PLI* > 5 (very highly polluted)	[39]
Er	$Er = Tr \times CF$	Er< 40 low risk; 40 <Er< 80 moderate risk 80 <Er< 160 considerable risk 160 <Er< 320 high risk Er> 320 very high risk	[38]
RI	$RI = \Sigma Er$	*RI* < 150 low ecological risk 150 <*RI*< 300 moderate ecological risk 300 < *RI* <600 considerable risk ecological *RI* > 600 very high ecological risk index	[38] [42]

Table (4) Comparison of metal concentrations (μg g^{-1} dry wt) in Sediments of the coast of Aden and other values in the region and the world

Locality	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
Aden coasts, Yemen	0.6-2.92 1.6	9.7-26.4 16.2	12.6-40.9 24.87	3.3-55.3 15.8	1061-3663 2772.7	47.8-394.6 214.85	3.9-30.3 14.5	13.6-46.9 28.15	32.3-97.2 54.7	Present study
Aden coasts, Yemen	0.93-3.3	18.4-42.4	135-389	11-120.6	285-1205	548-2250	13.6-30	ND-1350	62.3-381	[23]
Gulf of Aden, Yemen	-	13.8-33.6 23.97	17-233.9 82.19	8.09-111 19.89	2140-2769 2577.8	138-658.9 350.5	16.2-48.1 34.54	14.8-138.1 77.28	21.9–264 128.6	[18]
Hadhramout, Yemen	1.02-2.80	-	3.85-16.6	13.8-51.2	1255-3141	27.98-87.4	22.7-38.7	10.21-19.3	18.5-84.95	[9]
Red Sea, Yemen	0.2 0.7	6.3-15	6.8-7.6	3.6-.9	540-840	44.3-70.2	2.5-6.8	2.4-4.6	7.6-9.6	[48]
Akkah Beach, Abu Dhabi	0.09	45.5	303	3.31	29600	360	1010	1.3	-	[47]
Ras Al Yei, Oman	0,14	6.92	133	6.66	10700	209	77.8	0.449	11.4	
Red Sea, Egypt	2.48-8.14	-	1.39-75.3	5.36-48.9	1549.8-4729.8	54.9-966.4	9.5-67.04	10.78-70.37	30.1-99.8	[46]
Tuticorin coast, India	0.60-1.65	-	-	0.86-9.78	669-2071.8	63.6-91.6	-	-	10.3-17.94	[49]
Southwest coast, Spain	0.19-25	-	32-92	41-336	15900-35000	180-569	10-50	20-97	141-649	[45]

Table (5) The Enrichment Factor (*EF*) for heavy metals in Aden coast sediments

Site No.	Name of site	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
A1	Sira Island	56.51	12.49	5.17	5.13	5.32	3.71	20.66	11.59
A2	Abyan	30.31	7.04	3.41	3.32	2.65	2.29	11.17	4.83
A3	Labor Island	69.81	11.66	3.66	5.58	3.69	3.18	28.81	10.36
A4	Al- Hiswah	52.83	19.05	5.32	6.52	6.52	3.79	13.47	9.04
A5	al-Khissaa	140.95	13.93	3.69	10.91	1.48	0.88	23.95	8.72
A6	al-Ghadir	113.75	13.79	3.92	5.99	2.78	3.77	37.58	7.81
A7	Kobagen	249.84	33.84	11.75	8.06	13.60	5.84	55.23	20.93
A8	Fuqum	86.75	16.42	4.29	4.58	4.86	6.71	16.03	9.95
A9	Amran	160.96	18.70	7.27	4.61	3.89	5.00	35.79	15.39
Minimum		30.31	7.04	3.41	3.32	1.48	0.88	11.17	4.83
Maximum		249.84	33.84	11.75	10.91	13.60	6.71	55.23	20.93
Mean		106.86	16.32	5.39	6.07	4.98	3.91	26.96	10.96

Table (6) Geo-accumulation Index (*Igeo*) of heavy metals in Aden coast sediments

Site No.	Name of site	Zn	Pb	Ni	Mn	Fe	Cu	Cr	Co	Cd
A1	Sira Island	-0.87	-0.04	-2.51	-1.99	-4.4	-2.05	-2.03	-0.76	1.42
A2	Abyan coast	-2.01	-0.8	-1.47	-2.8	-4.28	-2.55	-2.51	-1.47	0.64
A3	Labor Island	-0.97	0.51	-0.80	-2.8	-4.34	-1.86	-2.47	-0.8	1.78
A4	Al-Hiswah	-1.56	-0.10	-0.47	-2.45	-4.72	-2.02	-2.31	-0.47	1.00
A5	al-Khissaa	-1.35	1.11	-0.67	-2.02	-4.47	-1.05	-2.58	-0.67	1.78
A6	al-Ghadir	-1.64	0.63	-0.82	-3.91	-4.60	-2.02	-2.63	-0.82	2.67
A7	Kobagen	-1.50	-0.09	-0.81	-3.13	-4.88	-2.88	-2.33	-0.81	2.23
A8	Fuqum	-1.20	-0.10	-0.48	-2.12	-4.51	-2.32	-2.41	-0.48	2.08
A9	Amran	-1.73	-0.50	-1,45	-2.23	-5.67	-3.47	-2.81	-1.44	1.95
Minimum		-2.01	-0.80	-2.51	-3.91	-5.67	-3.47	-2.81	-1.47	0.64
Maximum		-0.87	1.11	-0.47	-1.99	-4.28	-1.05	-2.03	-0.47	2.67
Mean		-1.43	0.07	-1.00	-2.61	-4.65	-2.25	-2.45	-0.86	1.73

Table (7) Quantification of contamination (*QoC*, %) values of metals in Aden coast sediments

Site No.	Sites Name	Zn [b]	Pb [a, b]	Ni [b]	Mn [b]	Fe [b]	Cu [b]	Cr [b]	Co [a, b]	Cd [a]
A1	Sira Island	-17.95	46.25 [a]	-73.75	-62.32	-92.89	-63.67	-63.39	-11.58 [b]	300.00
A2	Abyan coast	-62.84	-14.00 [b]	-82.35	-79.58	-92.27	-74.44	-73.72	45.79 [b]	133.33
A3	L. Island	-23.32	113.25 [a]	-76.47	-72.63	-92.57	-58.73	-72.94	13.68 [b]	416.67
A4	Al-Hiswah	-51.20	-23.50 [b]	-85.35	-63.00	-94.30	-83.35	-72.82	8.16 [a]	200.00
A5	al-Khissaa	-43.95	62.00 [a]	-95.95	-15.00	-93.21	-66.80	-77.50	5.79 [b]	853.33
A6	al-Ghadir	-54.15	132.25 [a]	-84.15	-82.81	-93.79	-83.34	-78.20	7.89 [a]	603.33
A7	Kobagen	-49.60	40.00 [a]	-89.94	-65.52	-97.45	-90.80	-73.20	14.21 [b]	533.33
A8	Fuqum	-37.90	5.30 [a]	-70.00	-68.09	-93.40	-86.45	-74.65	7.89 [a]	470.00

A9	Imran	-57.00	5.25 [a]	-90.00	-88.55	-97.05	-93.90	-80.75	45.00 [b]	373.33
Minimum		-62.84	-23.50 [b]	-95.95	-88.55	-97.45	-93.90	-80.75	45.79 [b]	133.33
Maximum		-17.95	132.25 [a]	-70.00	-15.00	-92.27	-58.73	-63.39	8.16 [a]	853.33
Mean		-44.21	40.76 [a]	-83.11	-66.39	-94.10	-77.94	-74.13	14.97 [b]	431.48

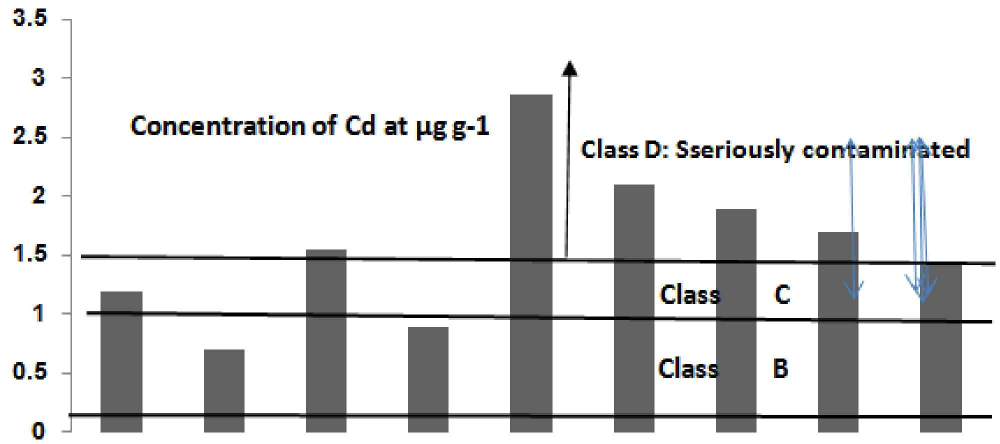
[a]anthropogenic magnitude; [b]geogenic source

Table (8) Contamination factor (*CF*), Degree of contamination (*Dc*) and Pollution Load Index (*PLI)* of heavy metal for the coasts of Aden

Sites	Sites	Contamination factor (C_f)								***Dc***	***PLI***
No.	Name	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn		
A1	Sira Island	4.0	0.88	0.37	0.36	0.38	0.26	1.46	0.82	8.53	0.7
A2	Abyan coast	2.33	0.54	0.26	0.26	0.20	0.18	0.86	0.37	5.0	0.42
A3	Labor Island	5.17	0.86	0.27	0.42	0.27	0.24	2.13	0.77	10.13	0.7
A4	Al-Hiswah	3.0	1.08	0.30	0.37	0.37	0.22	0.77	0.51	6.62	0.57
A5	al-Khissaa	9.35	0.94	0.25	0.74	0.1	0. 6	1.62	0.59	13.59	0.8
A6	al-Ghadir	7.03	0.85	0.42	0.70	0.17	0.23	2.32	0.48	12.2	0.73
A7	Kobagen	6.33	0.86	0.29	0.20	0.34	0.15	1.4	0.53	10.1	0.58
A8	Fuqum	5.7	1.07	0.28	0.30	0.32	0.44	1.05	0.65	9.81	0.69
A9	Imran	4.73	0.55	0.21	0.14	0.11	0.15	1.05	0.45	7.39	0.4
Minimum		2.33	0.54	0.21	0.14	0.1	0.15	0.77	0.37	5.2	0.4
Maximum		9.35	1.08	0.42	0.74	0.38	0.44	2.32	0.82	13.59	0.8
Mean		5.29	0.85	0.29	0.39	0.25	0.23	1.41	0.57	9.26	0.62

Table (9) The potential ecological risk index of heavy metals in the sediments of Aden coast

Sites No	Name of sites	Potential ecological risk (Er^a)								RI^b	Risk grade
		Mn	Zn	Pb	Ni	Cu	Cr	Co	Cd		
A1	Sira Island	0.38	0.82	7.3	1.9	1.8	0.74	4.4	120	137	Low
A2	Abyan coast	0.2	0.37	4.3	1	1.3	0.52	2.7	70	80	Low
A3	Labor Island	0.27	0.77	10.65	1.35	2.1	0.54	4.3	155	175	Moderate
A4	Al-Hiswah	0.37	0.51	3.85	1.85	1.85	0.6	5.4	90	104	Low
A5	al-Khissaa	0.1	0.59	8.1	0.5	3.7	0.5	4.7	281	299	Moderate
A6	al-Ghadir	0.17	0.48	11.6	0.85	3.5	0.84	4.25	211	233	Moderate
A7	Kobagen	0.34	0.53	7	1.7	1	0.58	4.3	190	205	Moderate
A8	Fuqum	0.32	0.65	5.25	1.6	1.5	0.56	5.35	171	186	Moderate
A9	Imran	0.11	0.45	5.25	0.55	0.7	0.42	2.75	142	152	Moderate
Minimum		0.3	0.37	3.85	0.5	0.7	0.42	2.7	70	80	Low
Maximum		0.38	0.82	11.6	1.9	3.7	0.84	5.35	281	299	Moderate
Mean		0.10	0.6	7.0	1.3	1.9	0.6	4.2	159	175	Moderate



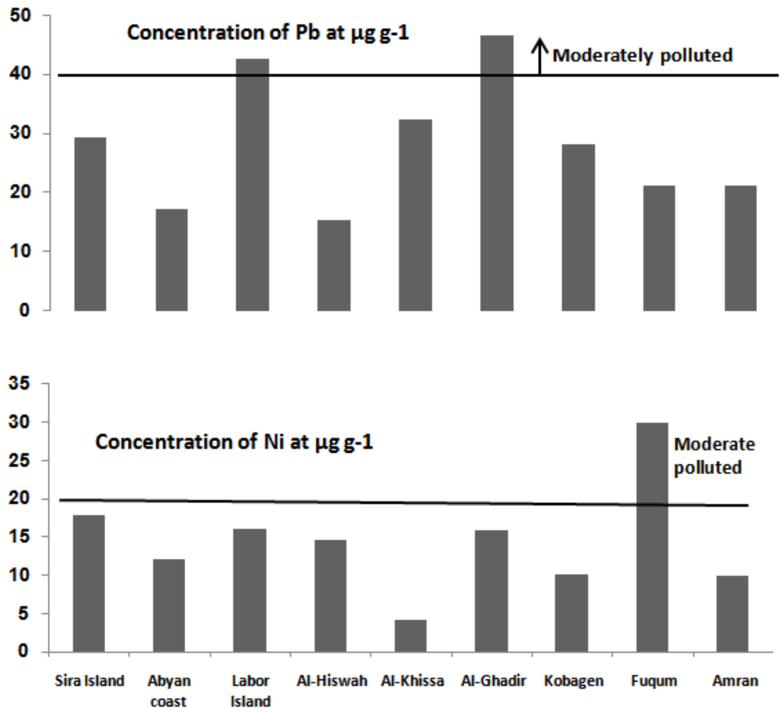


Figure 3: Average concentration of the Cd, Pb and Ni in the surface sediments of Aden coast

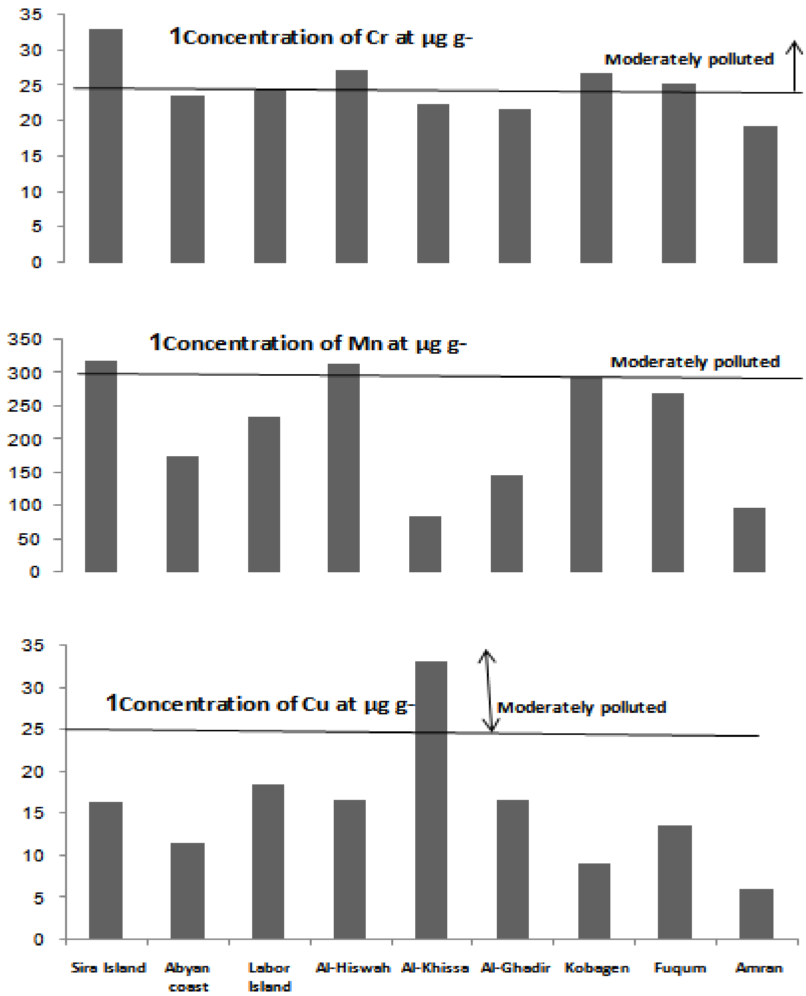


Figure 4: Average concentration of the Cr, Mn and Cu in the surface sediments of Aden coast

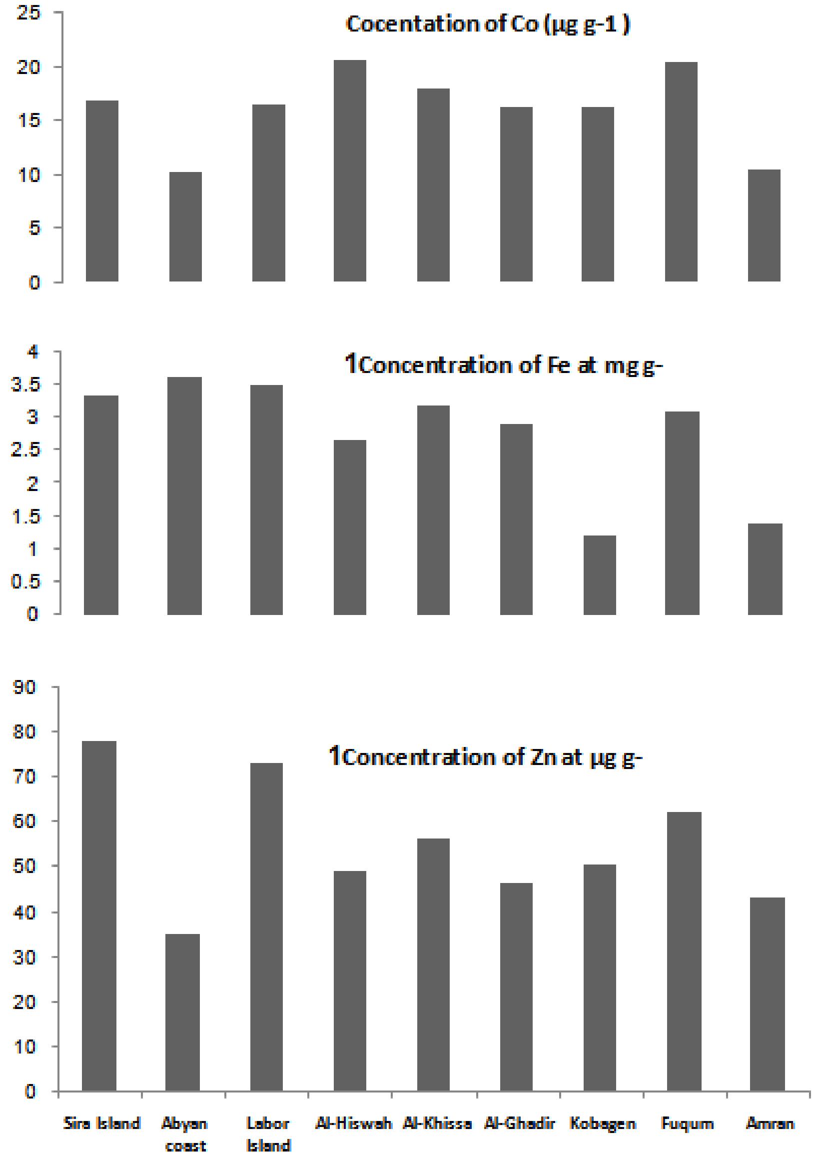


Figure 5: Average concentration of the Co, Fe and Zn in the surface sediments of Aden coast
Degree of Contamination, pollution load indices and risk index of Aden coast sediments

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